

Preparation of compact polyaniline films: electrochemical synthesis using agar gel template and charge-storage applications

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Abstract

Polyaniline (PANI) is electrochemically synthesized using agar gel as a template (Agar-PANI). The material characteristics and electrochemical behavior of the Agar-PANIs are compared with those of polyaniline synthesized by means of conventional methods (C-PANI). The electrochemical synthesis is monitored using the cyclic potential sweep (CPS) technique. The dependency of the total deposition charge on the number of cycles can be satisfactorily explained with a CPS parameter, n , and is consistent with scanning electron micrographs. The electrical conductivity and the bulk density of the Agar-PANI samples are 1.5 S cm^{-1} and 1.53 g cm^{-3} , which are three orders and four times larger than those of the C-PANI samples, respectively. On the other hand, C-PANI and Agar-PANI have similar crystallinity. The capacitances of the Agar-PANIs are $200\text{--}500 \text{ F cm}^{-3}$ at 5 mHz and these electrodes would be adequate for high energy density devices. The accommodation of glutamate is $1.5 \times 10^{-3} \text{ mol cm}^{-3}$ for the Agar-PANI, which is two orders of magnitude larger than when a polypyrrole electrode is used.

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1. Introduction

Polyaniline is an attractive conducting polymer due to its various potential applications such as batteries [1], electrochemical capacitors [2], corrosion protection [3], and electromagnetic shielding [4]. Polyaniline has a low conductivity, and a high doping level and stability. Polyaniline can be easily synthesized in both aqueous and non-aqueous solutions.

The doping level of polyaniline is about 40%, which is relatively high compared with other conducting polymers which have doping levels of under 30% [5]. Therefore, polyaniline is a promising material for charge-storage electrodes. Generally, polyaniline is highly porous when it is electrochemically synthesized. The ionic accessibility of a polyaniline electrode is better than other conducting polymers due to the high porosity, while it diminishes the charge capacity considerably. Control of the morphology of polyaniline is difficult and its variation is limited.

Active materials for batteries and electrochemical capacitors are required to have high specific energy and capacitance. High electrical conductivity is also necessary for electronic applications such as microelectronics. Many research groups have investigated technologies to control the electrical and electrochemical properties of conducting polymers. In one such trial, very compact films which were advantageous for charge storage could be obtained by adding a small amount of *p*-phenylene diamine (PPDA) to the electrosynthesis solution [6,7]. The template method has been widely used. In particular, porous media have been adopted by many researchers for this purpose. The template method is a very accurate and efficient tool for controlling morphology and ordering [8] which have direct effects on the electrical and electrochemical properties of conducting polymers. Porous membranes such as polycarbonate (PC) [8], anodic aluminum oxide (AAO) [9], silica gel and polyvinylidene fluoride (PVDF) [10,11] have been used as a template. In particular, a silica gel–polyaniline composite has been reported to be dense and to have high crystallinity and capacitance. On the other hand, conducting polymers synthesized with AAO membranes are fibers which are inappropriate as electrode materials. Polymer templates are difficult to dissolve completely after synthesis of conducting

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polymers. When conducting polymers are used as electrodes, the template material should be removed from the composite because it is electrochemically inactive and could decrease the ionic conductivity in conducting polymer films.

In this work, agar gel, an interconnected cellular material with relatively large pores (about 100 nm to 10 μm), is used as a template for polyaniline synthesis. Agar gel is attractive because it can be easily formed and removed. Its pore size can be controlled by changing the agar to water ratio in preparing the agar sol. Moreover, the interconnected pore structure would be a candidate for template synthesis of polyaniline with a continuous network, which is adequate for electrode materials. An investigation is made of the morphology, the degree of crystallinity, the electrical and electrochemical properties such as electrical conductivity and capacitance, and the amount of release of glutamate for polyaniline films synthesized using different methods.

2. Experimental

2.1. Preparation of electrodes

To obtain a smooth and reproducible surface, a thin film of gold was used as an electrode for polyaniline synthesis. The gold electrode was fabricated by rf sputtering or thermal evaporation. A bare Si-wafer (100, p-type, LG Siltron Inc.) was oxidized by the wet thermal method [12] to form an insulating SiO_2 layer with a thickness of 3000 Å. Chromium (200 Å) was deposited to this layer by rf magnetron sputtering or thermal evaporation, and deposition of the gold (500–700 Å) layer followed. Chromium was used as a buffer layer to enhance the adhesion between gold and SiO_2 .

2.2. Synthesis of agar gel film

A 5 wt.% agar solution was prepared by adding agar powder (Junsei Chem. Co., Ltd.) to double-distilled, de-ionized water. The mixture was heated to 90 °C with vigorous stirring; then, a thin-film electrode was dip-coated with the agar sol for 3 min. Gelation was proceeded at room temperature for 15 min.

2.3. Synthesis of polyaniline

Polyaniline was electrochemically synthesized on the gold electrode. A three-electrode set-up was employed; the working electrode was a bare gold electrode or an agar gel coated gold electrode, the counter electrode was the platinum plate, and the reference electrode was Ag/AgCl (sat'd KCl). All electrochemical experiments were performed with an EG&G model 273A potentiostat/galvanostat connected to a personal computer. Synthesis of polyaniline was carried out using a potentiodynamic method by cycling the potential at a scan rate of 50 mV s⁻¹. In the case of using agar gel as a template, agar gel was removed after the synthesis of polyaniline

by dipping the electrode in excess water at 90 °C for 20 min.

Prior to all experiments, dry nitrogen was bubbled through the electrolyte solution for 30 min, and all electrochemical tests were carried out under a dry nitrogen atmosphere. All reagents were used without further purification.

2.4. Characterizations

Fourier transform infrared (FT-IR) spectroscopy (Hi-resolution FT-IR spectrometer, 375 C, Bio-Rad) was carried out in order to detect agar residues. KBr was used as a transparent window.

To investigate the morphology of polyaniline samples, scanning electron micrographs (S4200, Hitachi) were obtained. The thickness of the samples were determined from the corresponding micrographs. The apparent densities of polyaniline samples were measured by a direct method: free-standing films of polyaniline were obtained by dissolving the underlying gold layer, and then weighing with a microbalance.

The electrical conductivities of polyaniline films were determined via the van der Pauw method [13,14]. After the gold layer was dissolved in an aqueous KI/I₂ solution, the resulting polyaniline film was attached by mild hot-pressing to the polyethylene film which acted as a support. Then, the polyaniline film was doped in 1 M H₂SO₄ solution and dried. The electrical conductivity was measured with two configurations: the commercial 4-in-line probe and the periphery probe [12–14]. For the periphery probe, electric wires and polyaniline films were connected with silver paste (Dotite electroconductives, Fujikura kasei Co.).

After polyaniline films were doped in 1 M H₂SO₄ solution for 24 h wide angle X-ray diffraction (WAXD) measurements were carried out using an X-ray diffractometer (RINT 2000, Rigaku). The CuK α radiation source was operated at 60 kV, 60 mA and the scan data were measured at 0.05° intervals with a scan speed of 4° per min. The scan range was 4–45° and all measurements were performed in the reflection geometry.

2.5. Electrochemical characterization and controlled release of glutamate with polyaniline electrodes

Using a frequency response detector (Model 1025, EG&G PARC), the ac impedance was measured with an ac signal of 5.0 mV_{rms} at a fixed biased voltage in a three-electrode cell using Ag/AgCl (sat'd KCl) as the reference electrode and a platinum sheet as the counter electrode in 0.1 M H₂SO₄ electrolyte.

Electrochemical doping (loading) and de-doping (release) of glutamate (Glu) acting as a neurotransmitter in the human body was carried out with the polyaniline electrodes. Doping of Glu was performed in a 0.05 M glutamic acid (99%, Aldrich)/0.1 M sodium glutamate (98%, Aldrich) aqueous solution at 0.5 V for 10 min, followed

by washing the polyaniline electrodes in 0.1 M NaCl solution. Glutamate was released in a fresh 0.1 M NaCl solution at -0.5 V for 10 min. The amount of Glu released was determined by amino acid analysis using high performance liquid chromatography (HPLC, T-series 1050 HPLC, Hewlett-Packard).

3. Results and discussion

Polyaniline films were synthesized using three different methods (Table 1). The conventional method is the direct electrochemical synthesis of polyaniline on gold electrodes without any template or additives (C-PANI). A modified method is electrosynthesis with a small amount of PPDA in the electrolysis solution (PPDA-PANI). Agar-PANI represents polyaniline films synthesized via the agar gel template method, as shown in Fig. 1.

Agar gel is electrically inactive and is used only as a template for polyaniline synthesis. Electro-inactive materials in a conducting polymer film might be an obstacle to ionic migration when the film is used as an electrode. Therefore, template material should be removed after the synthesis of polyaniline. Agar gel is appropriate as a template material because it can be easily dissolved. Its interconnected structure results in a polyaniline film with a continuous structure, which is adequate for an electrode material.

3.1. Characterization of template-synthesized PANI films

Agar gel can be dissolved in hot water (above 90°C). As agar gel makes a composite with polyaniline, however, its complete dissolution in hot water is questionable. Therefore, to confirm whether agar residue exists in the Agar-PANI electrode or not, FT-IR spectroscopy was car-

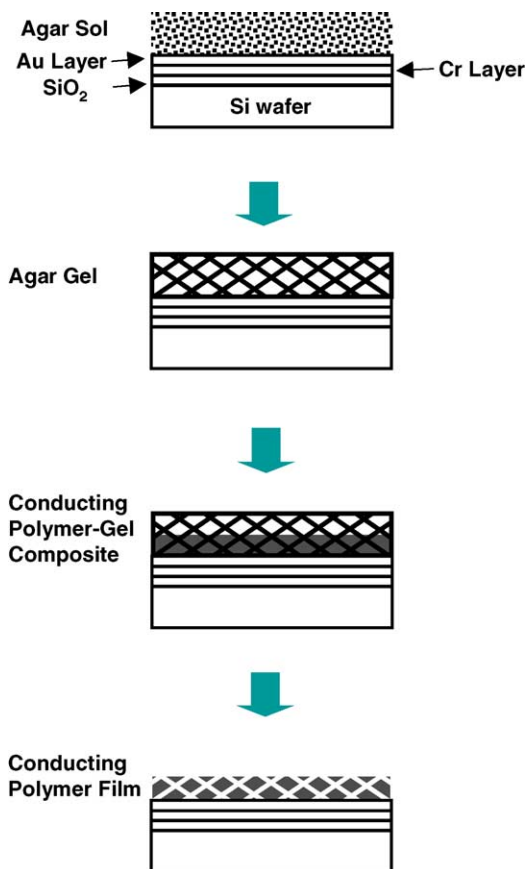


Fig. 1. Template method for conducting polymer synthesis.

Table 1
Preparation of polyaniline films using three different methods

Synthesis method	Code	Number of cycles (<i>N</i>)	Film thickness (μm)
Conventional	C-PANI1	10	3.4
	C-PANI2	20	14
	C-PANI3	30	28
	C-PANI4	40	37
	C-PANI5	50	50
	C-PANI6	60	60
Modified ^a	PPDA-PANI1	20	18
	PPDA-PANI2	30	21
	PPDA-PANI3	50	29
Agar gel template	Agar-PANI1	20	0.8
	Agar-PANI2	30	2
	Agar-PANI3	60	3.7
	Agar-PANI4	90	6.8
	Agar-PANI5	120	7.6

^a Polyaniline samples were electrochemically synthesized in 1 M HClO₄/0.5 M aniline/ 2.5×10^{-2} M PPDA aqueous solution by cycling the potential between -0.055 and 0.78 V at a scan rate of 50 mV s^{-1} .

ried out with three different samples, namely, agar, C-PANI and Agar-PANI (Fig. 2). Here, agar and C-PANI have been adopted as pure reference materials. Pure agar has the wide absorption bands of $3200\text{--}3600$, $2800\text{--}3000$ and $1000\text{--}1200 \text{ cm}^{-1}$ due to O–H stretching, C–H stretching and C–O–C stretching, respectively [15,16]. The C–O–C stretching absorption band can be observed only in a pure agar sample, because polyaniline does not have such chemical units. Therefore, these peaks are critical for detecting the residue of agar in the Agar-PANI film. The spectrum of pure polyaniline has four main absorption bands located at 1130 , 1290 , 1486 and 1580 cm^{-1} . These bands can be assigned to the SO_4^{2-} absorption, C–N–C stretching, benzene and quinoid ring vibration, respectively [17,18]. If there was any agar in the Agar-PANI, its spectrum would be different from that of the C-PANI and specific peaks of agar would appear in its spectrum. C–O–C stretching peaks of agar cannot be observed in Fig. 2. Therefore, little agar residue exists in the Agar-PANI film which has a very similar chemical structure to the C-PANI film.

Scanning electron micrographs of the C-PANI film are given in Fig. 3(a) and (b). The film is formed by a direct synthesis of polyaniline on the electrode surface without any treatment or additives. The C-PANI film is highly porous and fibrous. Its porosity and structure can be controlled by the anions used, though the variation is not much [6,19].

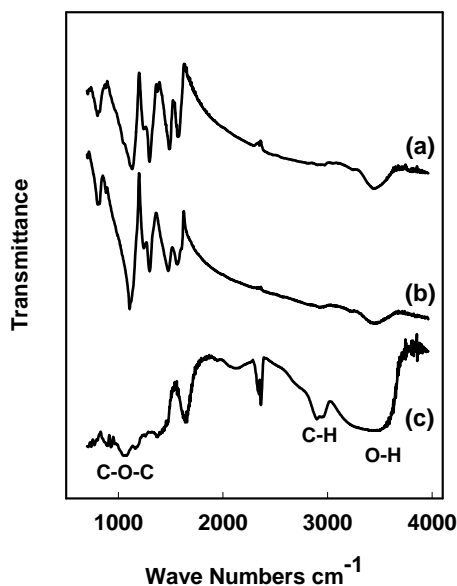


Fig. 2. FT-IR spectra of polyanilines synthesized with (a) agar gel template, (b) conventional method in 0.5 M H₂SO₄/0.1 M aniline aqueous electrolytes and (c) agar gel. FT-IR spectra of polyanilines were obtained after doping the polyaniline films in 1.0 M H₂SO₄ solution for 24 h.

Mailhe-Randolph et al. [6,7] proposed a new method to increase the density and change the structure. This produces densely-packed polyaniline films which would be advantageous as battery electrodes by adding a cross-linking agent

(PPDA) for polyaniline synthesis. Electron micrographs of a PPDA–PANI film synthesized by this method are shown in Fig. 3(c) and (d). The structure is more aggregated and globular than that of C-PANI, though PPDA–PANI was powdery when dried completely. Agar-PANI is much more densely packed (Fig. 3(e) and (f)) and, interestingly, its structure is not uniform throughout the thickness, contrary to the previous cases. The outer skin is relatively porous while the inner core is more densely packed, as can be clearly seen in the cross-sectional view given in Fig. 3(e).

Electron micrographs of the cross-sections and top views of Agar-PANI films with different thickness are presented in Fig. 4. The morphology changes dramatically as the film thickness increases. At the initial stage of the synthesis (Fig. 4(a)), the structure is somewhat porous and globular. It appears that the morphology is uniform throughout the thickness. As the film thickness increases, however, a denser region forms near the electrode (Fig. 4(c) and (e)). For a much thicker film, a dense layer is clearly seen (Fig. 4(g)). On the other hand, the outermost layers remain porous and are similar to each other, irrespective of the film thickness (Fig. 4(b)–(h)).

The above observations suggest that two processes proceed in the synthesis of Agar-PANI, namely, film growth and inner film densification. In the initial stage, outer film growth is more pronounced, probably due to the small thickness of the film. As the thickness of the film increases, the

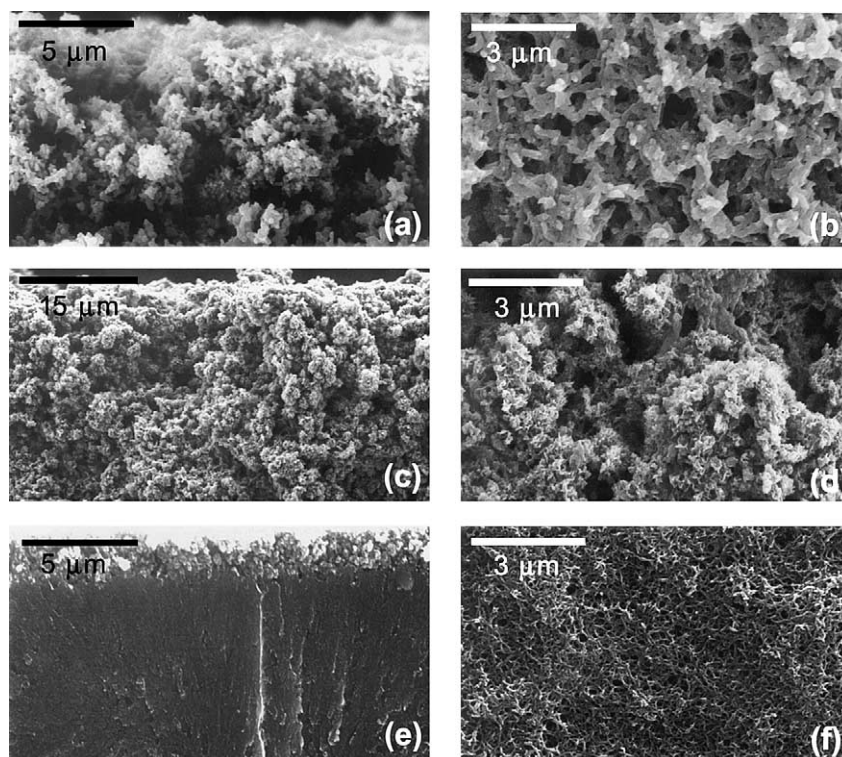


Fig. 3. Electron micrographs of polyaniline films synthesized with three different method. Polyaniline films were synthesized with the conventional method (C-PANI2, (a) and (b)), the modified conventional method (PPDA-PANI3, (c) and (d)) and the agar template method (Agar-PANI5, (e) and (f)) by cycling the potential between -0.055 and 1.045 V, except for the modified conventional case which had a potential range of between -0.055 and 0.78 V. In all cases, the scan rate was 50 mV s^{-1} (a), (c) and (e) are cross-sectional and (b), (d) and (f) are top views.

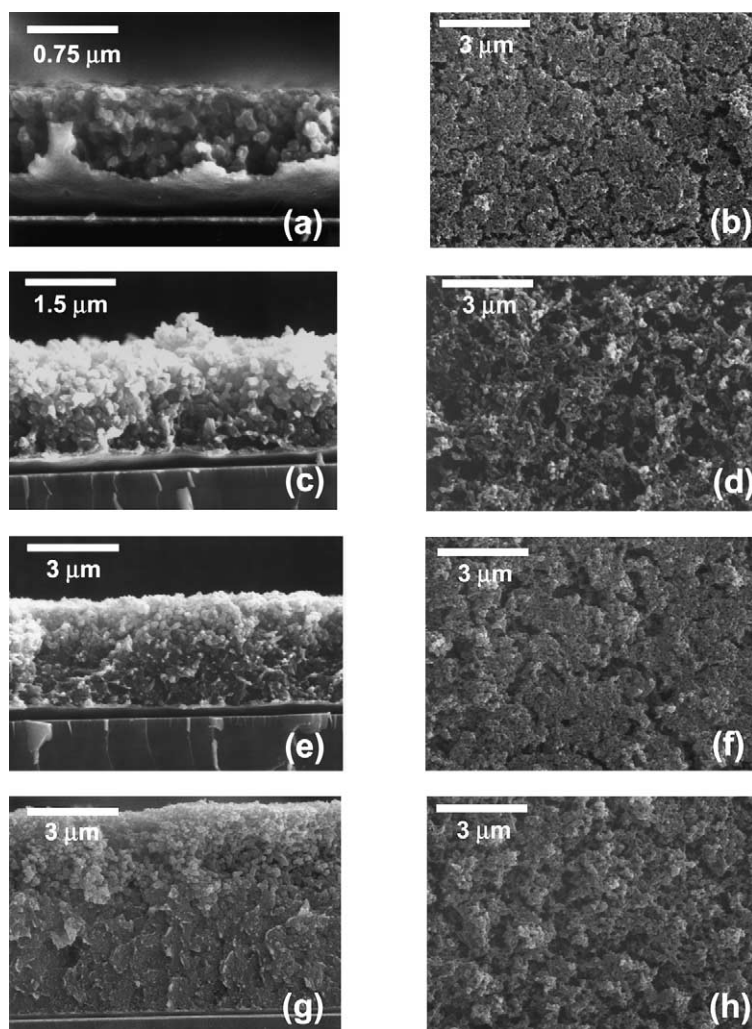


Fig. 4. Electron micrographs of polyaniline films synthesized with agar template method for different number of cycles by cycling the potential between -0.055 and 1.045 V at a scan rate of 50 mV s^{-1} . Number of cycles are 20 (Agar-PANI1, (a) and (b)), 30 (Agar-PANI2, (c) and (d)), 60 (Agar-PANI3, (e) and (f)) and 90 (Agar-PANI4, (g) and (h)), respectively. (a), (c), (e) and (g) are cross-sectional and (b), (d), (f) and (h) are top views.

presence of the dense layer becomes more noticeable. Zotti et al. [20] proposed an empirical equation which expresses the relationship between the synthesis charge of conducting polymers and the deposition conditions. For polyaniline synthesis, the following equation is formulated:

$$Q_i \cong \left(\frac{cN}{v} \right)^n \exp(aE_\lambda) \quad (1)$$

where Q_i is the accumulated deposition charge after the N th cycle finishes; c is the concentration of monomer; v is the scan rate; E_λ is the switching potential [21]. According to Zotti et al. [21] the value of n reflects the morphological characteristics of the resulting polyaniline film and is determined by the type of anion used for electropolymerization. That is, n would be 1 for large anions which stabilize large cations and decrease the solubility (class 1, CF_3COO^- ; BF_4^- ; and ClO_4^-) and 2 for the anions which can form soluble salts with the large cations such as cationic polyaniline oligomers (class 2, Cl^- ; NO^- ; and HSO_4^-).

The chronocoulogram for C-PANI synthesis when c is 0.1 M , v is 50 mV s^{-1} and E_λ is 1.045 V is shown in Fig. 5(a). The chronocoulogram shows second-order behavior ($n = 2$) with respect to time or N . To confirm the second power dependence of Q_i on the number of cycles, N , Q_i , versus N^2 is plotted for selected points in Fig. 6. A linear relationship exists between Q_i and N^2 and this shows that the HSO_4^- anions are class 2 anions. This result corresponds with that of Zotti et al. [2]. When polyaniline is synthesized using class 2 anions as supporting electrolytes, the resulting polyaniline films are known to have porous structures, and this feature is observed in Fig. 3(a).

The chronocoulogram for the Agar-PANI synthesis is shown in Fig. 5(b). The synthesis conditions were identical to the previous case, except that an agar gel coated gold film was used as the working electrode for the polyaniline synthesis. The behavior is different to that of the conventional case. Although HSO_4^- anions serve as supporting electrolytes, the behavior does not show second power

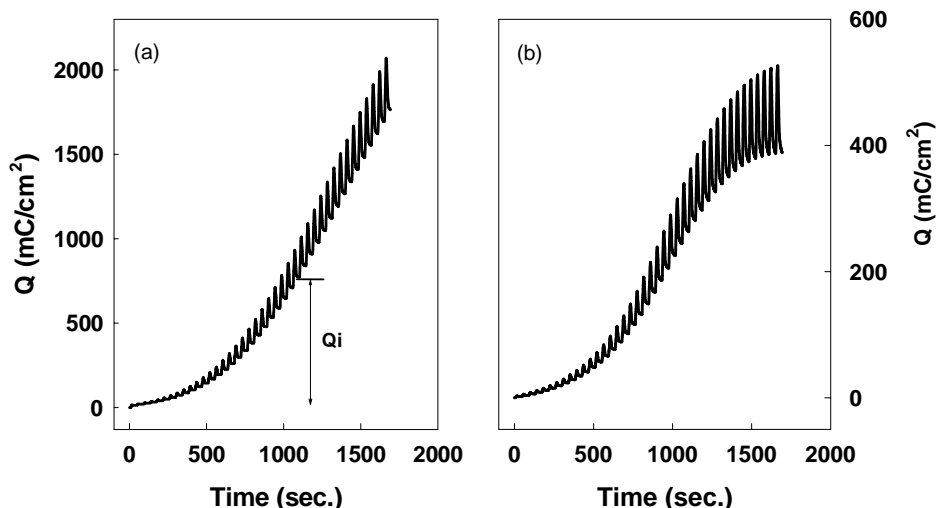


Fig. 5. Chronocoulograms during synthesis of polyanilines with (a) conventional and (b) agar gel template method in 0.5 M H₂SO₄/0.1 M aniline aqueous solution. Potential range was -0.055 to 1.045 V and the scan rate was 50 mV s⁻¹. After each cycle, the potential was kept at -0.055 V for 20 s to reduce fully the polyaniline films.

dependence of Q_i , on the number of cycles. Moreover, it cannot be fitted by one mathematical function, so that it is unable to be classified into either class 1 or class 2. In fact, the dependency of Q_i on N continuously changes as the synthesis proceeds. Therefore, the behavior of the deposition rate is divided into several regions (Fig. 7). At the initial stage ($N = 1-20$), Q_i increases linearly with N^2 , which means that the polyaniline synthesis belongs to the class 2 regime. At the second stage, the polyaniline synthesis belongs to the class 1 regime and Q_i increases linearly with N . At the later stages, the deposition rate decreases rapidly and the dependency on N continues to change. This tendency has not been reported previously in the literature [20,21].

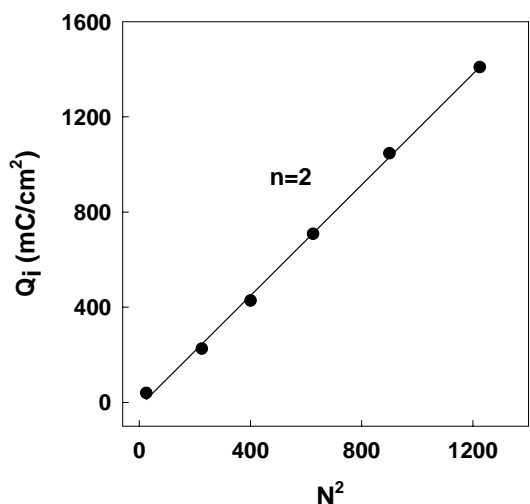


Fig. 6. Deposition charge vs. second power of number of cycles for polyaniline synthesis by the conventional method in 0.5 M H₂SO₄/0.1 M aniline aqueous solution. The potential range was -0.055 to 1.045 V and the scan rate was 50 mV s⁻¹.

Assuming the value of n is closely related to the morphology and the density of a film, the deposition behavior of Agar-PANI films is consistent with the electron micrographs of Fig. 4. A small value of n means that the film density is relatively high, while a large value corresponds to a porous and loosely-packed film. The polyaniline films synthesized without any additives or templates are porous and loosely-packed irrespective of the film thickness (not presented). This behavior can be explained by the fact that

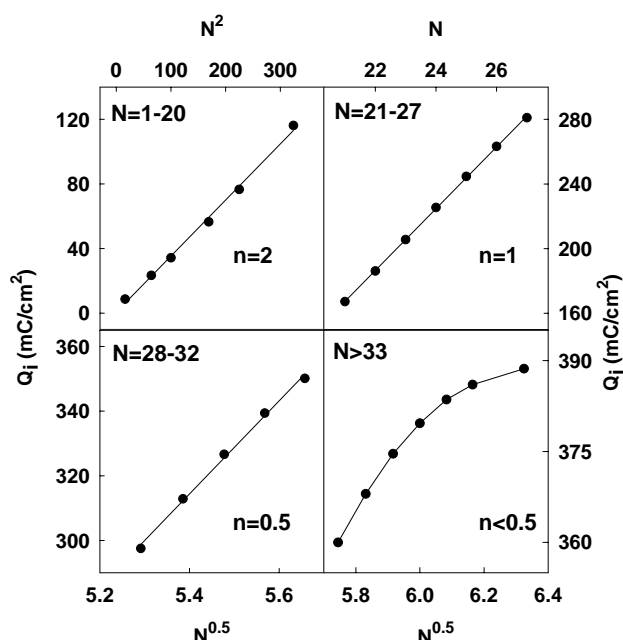


Fig. 7. Deposition charge vs. number of cycles for a polyaniline synthesis with agar gel template method in 0.5 M H₂SO₄/0.1 M aniline aqueous solution. The potential range was -0.055 to 1.045 V and the scan rate was 50 mV s⁻¹.

the second power dependence of Q_i on the number of cycles exists throughout the synthesis. On the other hand, the morphology of Agar-PANIs varies widely as the film thickness increased. Agar-PANI1 ($N = 20$) corresponds to stage I, and a porous film is observed in Fig. 4(a). The number of cycles of Agar-PANI2 ($N = 30$) corresponds to stage III. AgPANI2 shows the transition state between a porous film and a densely-packed film.

Agar-PANI3 and Agar-PANI4 belong to stage IV whose n value is under 0.5. Actually, these two films are non-porous and densely packed except the outmost layers. The n value should be assigned to either 1 or 2, according to the finding of Zotti et al. It is shown here, however, that n can have different values. In fact, n can change continuously during the synthesis.

The characteristics of the C-PANI and the Agar-PANI films are compared in Table 2. The most obvious difference between the two films is their bulk densities. As seen in the electron micrographs, density is a decisive factor in differentiating between the two methods. The density of the Agar-PANI was about four times larger than that of the C-PANI. The density of the C-PANI is consistent with the value given in the literature [2]. The electronic and electrochemical properties are heavily affected by the density of a polyaniline film. Template methods are known to align the conducting polymer chains into high crystallinity [9]. The crystallinity of two different films was calculated from XRD data by the integration of corresponding peaks. The XRD measurements were performed after doping of the samples in 1 M H_2SO_4 solution for 24 h. Contrary to expectation, the degree of crystallinity of the C-PANI is slightly higher than that of the Agar-PANI. The agar gel template has little effect on the alignments of polymer chains in polyaniline synthesis due to its relatively large pores (about 300 Å), though the small pores such as in an AAO or a silica gel template are known to enhance the alignment of the polymer chains.

The bulk electrical conductivity of Agar-PANI is three orders of magnitude larger than that of C-PANI. The results of two configurations (the 4-in-line and the periphery) were consistent to some extent. Electrical conductivity is one of the most important characteristics of conducting polymers and is affected by various parameters such as temperature and pressure, morphology, crystallinity, doping level, dopants, and pH of the doping solutions. Often, these parameters are correlated with one another in a complex manner

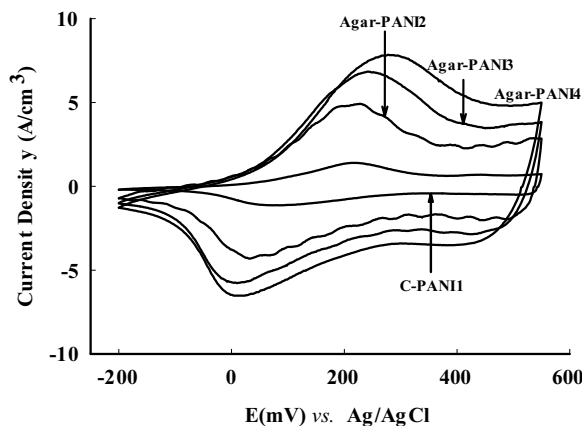


Fig. 8. Cyclic voltammograms of polyaniline films synthesized with conventional and agar gel template method. All voltammograms were obtained in 0.1 M H_2SO_4 solution at 5 mV s^{-1} .

[5]. Assuming that the doping parameters such as dopants, pH and doping level of the two polyaniline films are identical because the same doping conditions were applied, and considering that the crystallinity of the Agar-PANI is not enhanced by the agar gel template, it can be concluded that the difference in conductivity of the two films may originate from the morphology and the density. As the conductivity of the samples was measured without pressing or casting, it reflects the characteristics of the as-prepared polyaniline film. Therefore, in this case, the density (or the porosity) might significantly affect the bulk electrical conductivity.

3.2. Applications of template-synthesized PANI films

Conducting polymer electrodes have been widely used in energy-storage devices such as secondary batteries and electrochemical capacitors [1,2,22–24]. Their low charge capacity, however, has limited the development of practical devices using conducting polymers. Densely-packed polyaniline films are very useful in making energy-storage devices due to the high doping level and density. Cyclic voltammograms of the polyaniline films grown with two different methods are shown in Fig. 8. The current responses are presented as normalized with the volume of the polyaniline films. An increase in the volumetric current density is observed for the Agar-PANIs, which appears to be due to a decrease in the porosity or an increase in the density. In the case

Table 2

Comparison of characteristics for polyaniline films synthesized using two different methods

	Film thickness (μm)	Density (g cm^{-3})	Degree of crystallinity (%) ^a	Electric conductivity (S cm^{-1}) ^b	Capacitance (F cm^{-2}) ^c	Total amount of Glu released (mol cm^{-3})
C-PANI	7–8	0.36	8.0	$2.1\text{--}2.9 \times 10^{-3}$	95–105	8.0×10^{-4}
Agar-PANI	6–7	1.53	6.5	1.3–1.5	480–500	1.5×10^3

^a Calculated from X-ray diffraction pattern obtained after chemically doped in 1.0 M H_2SO_4 solution for 24 h.

^b Measured by van der Pauw method.

^c Measured at 5 mHz impedance spectroscopy.

of template synthesis, the current density increases as the total amount of polyaniline increases. The increase in current density for the Agar-PANI films might be due to the increase in film density. The portion of the loosely-packed outer region becomes trivial compared with the densely-packed inner region as the film thickness increases, since the thickness of the outer region remains unchanged during the synthesis. This morphological change would increase the film density, which is a significant determinant of current density. Note that the position of redox peak has shifted. It seems that the dense structure of the Agar-PANIs retards the ionic motion in an electrode, which results in a shift in the redox peak position. Because of their densely-packed structure, Agar-PANI films show high current density and low ionic conductance. The polyaniline electrodes with more open structures have low current density, while their ionic conductance would be higher. The current density and ionic conductance are closely related to the specific energy and specific power for electrochemical energy-storage applications such as batteries and electrochemical capacitors. To determine which property should be sacrificed depends upon the application [25].

To investigate further the electrochemical properties of polyaniline films, impedance spectroscopy was measured in aqueous 0.1 M H₂SO₄ solution. The frequency dispersion of two capacitance of polyaniline electrodes is shown in Fig. 9. Two synthesis methods show very different behaviors with respect to film thickness. For the C-PANI electrodes, the maximum capacitances are almost the same as each other. This behavior may result from the same film density irrespective of the film thickness. On the other hand, film thickness affects the electrodynamic behavior of the C-PANI films due to the different length of the ion transportation path. This is confirmed by a decrease in the stable capacitance region as the film thickness increases.

The impedance behavior of Agar-PANI electrodes is very different from that of C-PANIs. At very low frequencies (<10 mHz), the capacitance increases with film thickness. The capacitance at very low frequencies represents the maximum induced capacitance which is unaffected by the structural and morphological properties. Therefore, the maximum capacitance will be a sole function of the density of a material if the same analysis conditions are adopted. As discussed above, the density increases with the film thickness for Agar-PANIs. Therefore, the volumetric capacitance at very low frequencies increases with the density change. Note that the maximum capacitance exceeds 500 F cm⁻³ for the Agar-PANI5 film.

A porous electrode which has a good electrodynamic property has a long stable capacitance region. The stable region with high capacitance decreases with increasing film thickness of the Agar-PANI. This behavior has also been observed with C-PANI films, but is more pronounced in Agar-PANIs. Good electrodynamic properties come from a good ionic accessibility to the electro-active materials. In a thick and densely-packed electrode, ion migration would be significantly retarded. For the Agar-PANI films, as the film thickness increases, the film density also increases. These two effects significantly deteriorate the electrodynamic properties of Agar-PANI electrodes with increasing thickness.

From a practical view, it is necessary to consider two characteristics of electrodes, namely, charge capacity and electrodynamic properties. As a battery electrode, charge capacity would be a decisive factor, while power density should be preferentially considered as a capacitor electrode. As a battery electrode, Agar-PANI electrodes are advantageous because their capacities are about three to five times larger than those of C-PANI electrodes. Considering an electrochemical capacitor application, Agar-PANI electrodes seem to be disadvantageous due to their dense structures. For C-PANI1 and Agar-PANI3 electrodes of the same thickness, however, although the stable region of Agar-PANI3 in the capacitance–frequency plot is shorter than that of C-PANI1, the capacitances of Agar-PANI3 are still much larger than those of C-PANI1 up to 10 Hz. From these investigations, it is suggested that, as both battery and electrochemical capacitor electrodes, Agar-PANI would be

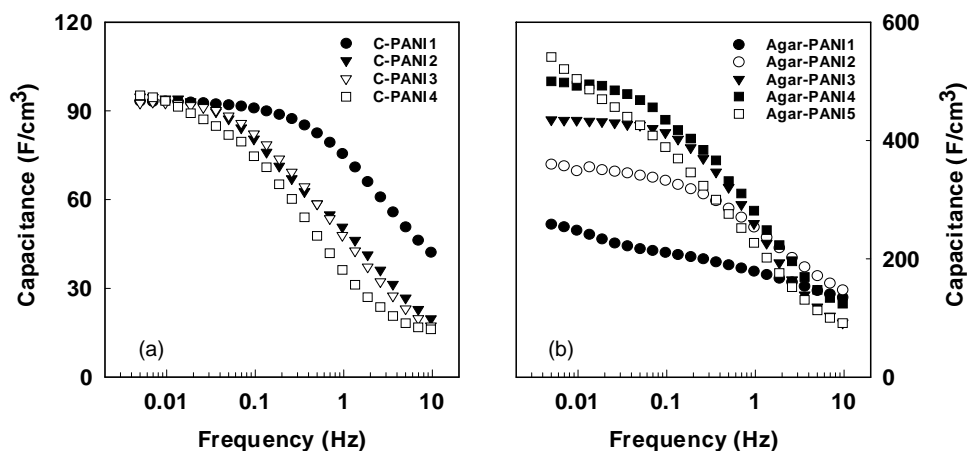


Fig. 9. Frequency dispersions of capacitance of (a) C-PANI and (b) Agar-PANI electrodes. All ac impedances were obtained in 0.1 M H₂SO₄ solution at their open-circuit potentials with an ac signal of 5 mV_{rms}.

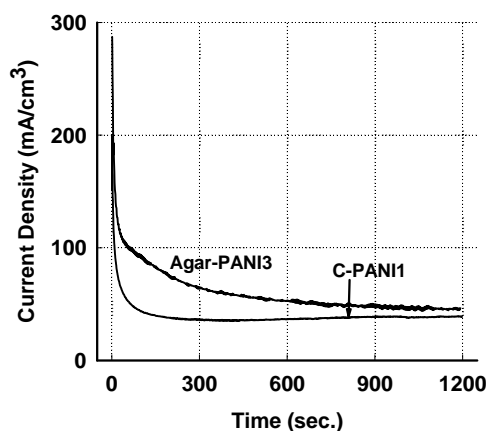


Fig. 10. Electrochemically stimulated release of Glu from polyaniline films grown with two different methods. Doping was performed at +0.5 V for 1200 s in Glu solution; de-doping (release of Glu) at -0.5 V for 1200 s. The time '0' refers to the starting point for application of de-doping potential.

an attractive material. In particular, Agar-PANI electrodes are very promising electrodes for micropower systems because of the high density and high capacitance.

Space-saving electro-active materials are required in many other applications. As a demonstration of the usefulness of compact polyaniline films, controlled release of Glu which plays an important role as a neurotransmitter in the nervous system is presented here. In this experiment, an electrically stimulated release of Glu was adopted because Agar-PANI films possess large capacitances. The electrochemically controlled release of Glu with a polypyrrole membrane has been reported by other groups [26,27]. With a similar experimental scheme, polyaniline has been examined in the present study as an electro-active material for Glu release. The Agar-PANI film shows larger accommodation for Glu than the C-PANI film (Table 2). The de-doping behavior of two polyaniline films for Glu release are shown in Fig. 10. The release of Glu from the C-PANI film is pulse-like, which might be due to the porous structure of the film. The release behavior of the Agar-PANI film is also pulse-like, but somewhat retarded. The total amount of Glu released from the Agar-PANI film is about double that of the C-PANI film. Nevertheless, the difference in Glu accommodation between two films is not as obvious as in the H_2SO_4 case. The relatively small difference may be due to the low electrical conductivity of polyaniline in the Glu solution which has a pH of about 4.3. It has been reported that an increase in pH from 0 to 5 will lower the electrical conductivity by nine orders [28]. It is suggested that the conductivity of a polyaniline electrode decreases by several orders at high pH and the electroactivity of the two polyaniline films is deteriorated, which would narrow the capacity difference for Glu. The amount of release for the polyaniline electrodes is one or two orders larger than that of a PPy electrode. The amount of Glu released from a PPy electrode is $5.4 \times 10^5 \text{ mol cm}^{-3}$ (calculated from [26]).

Controlled release of drugs in vivo requires a very small sized microsystem because it should be operated in a narrow blood vessel, a tissue, etc. Therefore, integration of components is one of the most important factors. For this reason, the high Glu accommodation of Agar-PANI film might assure the advancement of this technology.

In summary, polyaniline has been potentiodynamically synthesized using agar gel as a template. The electrochemical synthesis has been monitored using the cyclic potential sweep (CPS) technique. The dependency of the total deposition charge on the number of cycles can be satisfactorily explained with a CPS parameter, n , and is consistent with the features shown in electron micrographs. The n value is 2 at the initial stage of the synthesis, but the decreases continuously to a number smaller than 0.5. An n value less than 1 means that the polyaniline film is highly concentrated and densely packed. The electrical conductivity and the bulk density of the Agar-PANI samples are 1.5 S cm^{-1} and 1.53 g cm^{-3} , as which is three orders and four times larger than those of the C-PANI samples, respectively. The crystallinity, however, is about the same for the C-PANI and the Agar-PANI. The capacitances of the Agar-PANIs are $200\text{--}500 \text{ F cm}^{-3}$ at 5 mHz, and these electrodes would be adequate for devices with high specific energy. The accommodation of glutamate is $1.5 \times 10^{-3} \text{ mol cm}^{-3}$ for the Agar-PANI, which is two orders of magnitude larger than when a polypyrrole electrode is used. The Agar-PANI electrode developed here is promising as an electrode for secondary batteries, electrochemical capacitors and drug-delivery systems in vivo, especially for micro-sized apparatus such as MEMS and microrobots.

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